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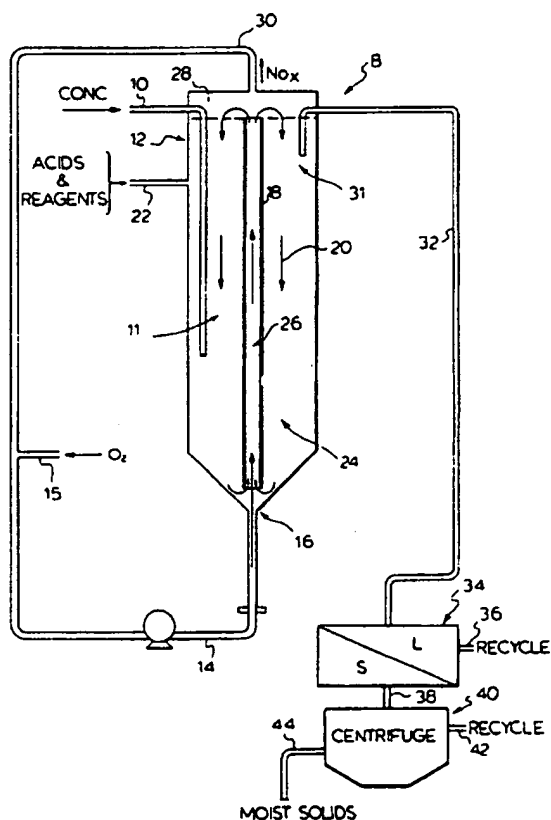
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<p>(21) International Application Number: PCT/CA94/00034 (22) International Filing Date: 24 January 1994 (24.01.94) (30) Priority Data: 009,844 27 January 1993 (27.01.93) US (71) Applicant: R & O MINING PROCESSING LTD. (CA/CA); c/o Westmin Resources Limited, Suite 904, 1055 Dunsmuir Street, Vancouver, British Columbia V7X 1C4 (CA). (72) Inventor: O'BRIEN, Robert, N.: 2614 Queenswood Drive, Victoria, British Columbia V8N 1X5 (CA). (74) Agent: WOODLEY, John, H.: Sim & McBurney, 330 Univer- sity Avenue, Suite 701, Toronto, Ontario M5G 1R7 (CA).</p>	<p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.</p>	

(54) Title: HYDROMETALLURGICAL RECOVERY OF METALS FROM COMPLEX ORES

(57) Abstract

A continuous hydrometallurgical process for conversion of ore derived copper and/or zinc sulfides into recoverable water soluble sulfates is provided. The process comprises: i) contacting the ore derived copper and/or zinc sulfides with sulfuric acid and with nitric acid to form a reaction mixture in an acidic solution, ii) maintaining the reaction mixture at a temperature in the range of 110 °C to 170 °C while continuously mixing the reaction mixture, iii) adding sufficient sulfuric acid and nitric acid to the reaction mixture to form a light precipitate and a dark precipitate in the reaction mixture, the light precipitate comprising water soluble sulfate salts of copper sulfate, zinc sulfate and iron sulfate, and the dark precipitate being water insoluble and comprising mainly elemental sulfur and gangue, iv) introducing a source of oxygen to the reaction mixture to promote oxidation in the presence of the nitric acid, of the sulfides to sulfates and to oxidize gaseous NO_x reaction products to regenerate nitric acid for the reaction mixture, v) removing the light and dark precipitates and any entrained acidic solution from the reaction mixture, vi) separating the light and dark precipitate from the acidic solution in preparation for treatment of the light precipitate for recovery of copper sulfate and/or zinc sulfate from the light precipitate, and vii) recycling the acidic solution to the reaction mixture.



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**HYDROMETALLURGICAL RECOVERY
OF METALS FROM COMPLEX ORES**

FIELD OF THE INVENTION

5 This invention relates to a hydrometallurgical process for conversion of copper and/or zinc sulfides in various copper containing ores such as chalcopyrite, into precipitates of their corresponding sulfates which can be subsequently readily recovered.

10 **BACKGROUND OF THE INVENTION**

 There is a significant push to develop commercial forms of a hydrometallurgical process to recover various types of metal from ore bodies. The significant advantage of a hydrometallurgical process over the
15 standard smelting process, is the significant reduction in sulfur dioxide emissions. Although the chemistry might appear to be relatively direct in extracting, for example, copper and zinc from sulfide ores, all known commercial approaches in this regard have either failed
20 or are not economically viable. It is known that several of these hydrometallurgical processes for leaching copper, zinc and the like from either ore concentrate or a rich ore involve the use of sulfuric acid and/or nitric acid and/or nitrate salts.

25 United States Patent 3,888,748 discloses a metal recovery process whereby copper may be recovered from sulfide ore concentrates containing minerals such as chalcopyrite (CuFeS_2). The copper is recovered by contacting the ore concentrate with a dilute aqueous
30 solution of nitric acid and sulfuric acid to give a leachate containing in solution of copper salts and iron salts and a residue. The leachate is subjected to further processing in which copper is recovered and iron is precipitated as jarosite. Jarosite has no value and
35 can complicate the recovery process. The nitrate ions and its derivatives must be substantially removed from the leachate to facilitate an electrowinning of copper or zinc from the solution.

In United States Patent 3,910,636 a process is disclosed for in-situ mining. Holes are drilled into an ore body and the holes are filled with an acid leaching solution containing nitrate ions at a pH range of 0.2 to about 2.0. However, the solution becomes diluted and hence, the process is relatively slow in leaching copper from the ore. In addition, the process cannot normally be used in limestone formations.

Another in-situ chemical mining process is disclosed in United States Patent 3,912,330 which is specifically directed at dealing with copper porphyry ores. Catalytic amounts of nitrate ion are added to an oxygenated sulphuric acid leach medium to improve the rate of copper extraction from copper sulfide ores. The nitrate concentrations may range from 0.05 to 0.50% and the acid media is oxygenated at oxygen pressures from 25 psi to 200 psi. Jarosite is said to be precipitated and the process is acknowledged to be unsuitable for surface heap leaching.

United States Patent 4,647,307 teaches that complex copper ores can be treated with oxidizing acid media. Arsenical ores can be processed especially well with this system.

Published literature in the field includes a Ph.D. dissertation (G. Van Weert, Ph.D. Dissertation, De Technische Universiteit, Delft, Holland, 1989) which contains an Appendix giving a summary of treatments for complex ores and concentrates containing chalcopyrite. Avramides et al (Hydrometallurgy, 5, 325-36 (1980)) describe a process in which the chalcopyrite leaching process consists of leaching with acetonitrile solutions of cupric and cuprous ions. Kiknadze et al (Izv. Akad. Nauk Gruz. SSR, Ser. Khim., 6 363-6 (1980)) describe a ferric ion leach of chalcopyrite where the ferric ion is regenerated with chlorine. Another ferric ion leach is described by Tkacova and Balaz (Hydrometallurgy, 21 103-12 (1988)) purports to increase the surface area of

chalcopyrite but mentions also that the sulfur on the surface retards the dissolution of the chalcopyrite. Pomanianowski et al. (Electrocatal., Mater. Symp. Electrochem. Sect. Pol. Chem. Soc., 9th meeting date 5 1987, 241-7, Edited by Pawel Nowak, Pol. Chem. Soc.: Warsaw Pol.) found that deposition of minor amounts of silver on the surface of chalcopyrite catalyzed the rate of dissolution by electrochemical means.

10 The above processes however are inadequate from one or more of the following perspectives:

- i) the processing cost is uneconomical relative to the value of the metals recovered,
- ii) inoperable in a commercial scale,
- iii) polluting off gases,
- 15 iv) inefficient recovery of the valuable metal(s),
- v) off gases cannot be treated for recycle and re-use in the process,
- vi) processing conditions require the use of pressurized reactors to obtain conversions of
- 20 copper and zinc sulfides to corresponding sulfate salts.

The process according to this invention overcomes several of the above problems in providing a process which does not have to operate under pressurized 25 conditions. Because of the use of high concentrations of sulfuric acid in the presence of oxidizing nitric acid and oxygen gas, the desired metals are recovered as water soluble salts precipitated in the acidic solution of the reaction mixture which is operated at temperatures in the 30 range of 110°C to 170°C at which temperature and high acidity the water soluble metal salts are less soluble.

SUMMARY OF THE INVENTION

According to an aspect of the invention a continuous hydrometallurgical process is provided for conversion in 35 the presence of nitric acid of ore derived copper and/or zinc sulfides into recoverable precipitates of their

corresponding sulfates while minimizing emissions of nitrogen gas and N_2O gas, The process comprises:

- i) contacting the copper and/or zinc sulfides obtained from said ores with sulfuric acid and with
5 nitric acid to form a reaction mixture in an acidic solution,
 - ii) maintaining the reaction mixture at a temperature in the range of $110^{\circ}C$ to $170^{\circ}C$ while continuously mixing the reaction mixture,
 - 10 iii) adding sufficient sulfuric acid and nitric acid to the reaction mixture to form a light coloured precipitate and a dark coloured precipitate in the reaction mixture, the light precipitate comprising water soluble sulfate salts of copper sulfate and/or zinc
15 sulfate and the dark precipitate being water insoluble and comprising sulfur and gangue,
 - iv) introducing a source of oxygen to the reaction mixture to promote oxidation in the presence of the nitric acid, of the sulfides to sulfates and to oxidize
20 gaseous NO_x reaction products to regenerate nitric acid for use in the reaction mixture,
 - v) removing the light and dark precipitates and any entrained acidic solution from the reaction mixture,
 - vi) separating the light and dark precipitate from
25 the acidic solution in preparation for treatment of the light precipitate for recovery of copper sulfate and/or zinc sulfate from the light precipitate, and
 - vii) recycling the acidic solution to the reaction mixture.
- 30 According to another aspect of the invention, the copper and/or zinc sulfides are provided in a finely divided ore concentrate, particularly an ore concentrate derived from an ore body of chalcopyrite, sphalerite and other sulfide or sulfo salt minerals. The copper sulfide
35 present in the sulfide ore ($CuFeS_2$) is converted by the process to partially dehydrated white copper sulfate,

which in the acid solution, precipitates and thereby forms part of the light coloured precipitate.

According to another aspect of the invention, the amount of sulfuric acid maintained in the reaction mixture is based on a volume concentration of concentrated sulfuric acid to volume of reaction mixture in the range of 35% to 65% volume per volume. The concentration of the nitric acid is at least 1.5 moles of nitric acid per mole of copper sulfide in the ore concentrate.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic of a flow diagram in which the process of this invention is carried out.

DETAILED DESCRIPTIONS OF THE PREFERRED EMBODIMENTS

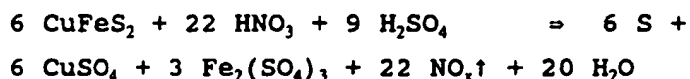
The process of this invention is particularly suited in the treatment of metal ores which contain copper sulfides and/or zinc sulfides. The ore may be either in a finely divided concentrate form, a finely divided rich ore or a combination of the two. Examples of such mineral bearing ores commonly include chalcopyrite, chalcocite, bornite, tetrahedrite, sphalerite, galena, molybendite, pyrite, pyrrhotite and arsenopyrite. The process is also equally applicable to the recovery of copper or zinc from these ores depending on whether such ores contain copper or zinc. The ore is in particle form and is preferably ground such that 75% of the finest particles pass 275 mesh. This ensures a finely divided material on which the reagents used in the process of this invention react. Most copper and/or zinc ore sources normally include chalcopyrite, sphalerite, bornite, pyrite, galena and mixtures thereof. Alternatively, the process of this invention may be applied to previously treated ores which may now be enriched in either copper or zinc. For example, an ore containing copper and zinc may be treated to preferentially remove some of the zinc and thereby

provide an ore enriched in copper. Hence the process would be used to remove copper from this treated ore.

In a preferred aspect of the invention the objective is to recover the copper and/or the zinc where such
 5 recovery may be firstly in the form of a water soluble precipitate containing zinc and/or copper in the sulfate form and then by further processing, the zinc and/or copper ions in solution may be refined to provide copper and/or zinc in separate electrowinning processes.

10 It is also appreciated that such ores may include precious metals such as rhodium, palladium, platinum, silver and gold. Usually such constituents are in trace amounts and may not warrant recovery. It has been found that these precious metals do not present a problem with
 15 respect to the processing conditions. Similarly, small amounts of Pb, Cd, As and Sb are commonly found in such ores. It has also been found that the presence of iron in the ore also does not present any processing problems and furthermore if desired, iron could also be recovered
 20 from the reaction products of this conversion process.

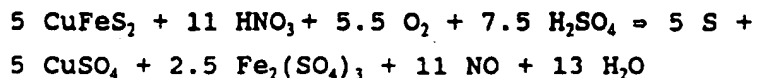
Although the chemistry in this conversion process involving the use of very high concentrations of sulfuric acid and the necessary amount of nitric acid is not fully understood, it is thought that the reaction could be
 25 generally demonstrated as follows in respect of recovering copper from a copper bearing ore:



30

It has been found that conversion of the emitted NO_x gases to nitric acid can be effected by the introduction of an oxygen containing gas to the reaction system. In this event, the general reaction scheme is thought to be:

35



Correspondingly the reaction involving zinc sulfide is thought to be in respect of recovery of zinc from a zinc bearing ore:



It is understood that these reaction schemes are of a general nature and the stoichiometry of the scheme may vary from that depicted. The following examples however
10 demonstrate the formation of the copper and iron sulfates which are part of the precipitate and that primarily NO and NO₂ gases are generated, which in the presence of oxygen are converted back to nitric acid and nitrous acid (HNO₃ and HNO₂). There are minimal emissions of the
15 environmentally undesirable N₂O gases.

The role that the nitric acid plays in this conversion process is not fully understood. It is thought that the nitric acid may in some way catalyze the conversion of the sulfur and iron moieties to their
20 higher valency states. It has been found that in accordance with this invention, the amount of off gases which can be converted back to or recycled as nitric acid is quite high and normally exceeds 80% and may be as high as 90%. The remaining nitrogen based off gases include
25 nitrogen and nitrous oxide which may make up the remaining 10 to 20%. Of that mixture, nitrous oxide is the lower in concentration, normally in the range of less than 5% of total nitrogen containing gases. As required for environmental purposes, the off gases containing the
30 nitrous oxide may be treated in the necessary manner before release to atmosphere.

It has been found that the amount of nitric acid used in the conversion process can vary considerably. It has been found that excessive amounts of nitric acid may
35 be used with little, if any impact on the overall efficiency of the process. There is however required a minimum amount of nitric acid to ensure this conversion

of the zinc and copper sulfides to sulfates which result in the form of the light precipitates. According to a preferred embodiment of the invention, the nitric acid concentration should be at least about 0.5 mole of nitric acid per mole of copper sulfide in the incoming concentrate or ore. Based on investigations with respect to the preferred embodiments, it has been found that a concentration of nitric acid in excess of 3 mole per mole of copper sulfide does not appear to enhance in any way the conversion of the sulfides to the sulfates. The preferred concentration for nitric acid is in the range of 0.5 to 1.5 mole of nitric acid per mole of copper sulfide. It has also been found that when the nitric acid is added to the reaction mixture it is preferable to add the nitric acid over time rather than an immediate introduction. The rate of addition may be based on the volume of reaction mixture. The rate of introduction of nitric acid may be in the range of 0.3% to 1% volume of nitric acid per minute based on the volume of reaction mixture and the time desired for the reaction.

The sulfuric acid is normally already in the reaction mixture and is maintained at a concentration at least in excess of 35% volume per volume of reaction mixture and upwardly to 65% volume per volume of reaction mixture in the manner demonstrated in the following Example 1. It has been found that the concentration of sulfuric acid being less than 40% volume per volume does not produce sufficient conversion of the sulfides and sulfates to produce the light precipitate and achieve the solid-liquid separation. Whereas, use of sulfuric acid in excess of 65% tends to create hazardous NO_x fumes in the light precipitate when re-dissolved. The reaction mixture is preferably maintained at about 10 M. At this acid concentration, the water soluble sulfates of copper, iron and zinc are predominantly insoluble to form the precipitate in this acidic mixture. It is also understood that in the continuous reactor the nitric acid

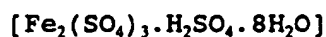
and the sulfuric acid are added essentially on a continuous basis or on an intermittent basis to maintain the desired concentrations of sulfuric acid in the reaction mixture and as well to maintain the molar relationship of the nitric acid to moles of incoming copper and/or zinc sulfides. It is appreciated that concentrations of sulfuric acid may be expressed in other units, such as 9% H_2SO_4 by weight of solution. For purposes of comparison, 35% v/v equivalent to approximately 50% by weight. At the upper end, 65% v/v is equivalent to 77% by weight. Other intermediate values include 40% v/v \approx 55% by weight and 50% v/v \approx 64.5% by weight.

It has been found that with increasing sulfuric acid concentrations, the amount of the precipitate in the light form increases, and as well the dark form which contains not only sulfur but as well gangue. Furthermore, by increasing the sulfuric acid concentration it has been found that more of the iron is precipitated in the light precipitate and as well, more of the copper and zinc move into the white precipitate than remain in solution. Also, there is a slight increase by weight in the amount of iron, copper and zinc which moves over into the dark precipitate at the higher concentrations of sulfuric acid. Therefore, depending upon the process parameters, the concentration of sulfuric acid may be adjusted within the range of 40 to 65% volume per volume to achieve the optimum recovery of at least the copper and zinc in the light precipitate.

It has been found extremely beneficial to this invention that the light precipitate is water soluble whereas the dark precipitate is soluble in organic solvents. This permits the water extraction of the desired metal sulfates from the light precipitate without in any way extracting any meaningful amounts of impurities from the dark precipitate. Furthermore, it avoids the use of organic solvents in attempting to

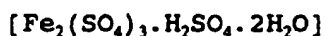
remove any of the dark precipitate before proceeding with the water extraction of the valuable metals from the light precipitate.

Although it is difficult to predict with varying acid concentration the moietic structure of the iron, copper and zinc materials in the precipitate, it is believed that with higher concentration of acid and/or at higher temperatures, the various salts tend to dehydrate. In their hydrated form, iron, copper and zinc may appear with or without entrapped NO_3^- as:



15

At higher concentrations of acid and/or temperature, the salts tend to dehydrate to produce



20



Hence, in a continuous reactor where the sulfuric acid concentration and the temperature may vary, the salts of the iron, copper and zinc may be hydrated and/or partially or totally dehydrated during processing as they remain in the light coloured precipitate. In any event, the dissolved forms of the copper, zinc and iron in the acid solution are eventually recycled in the process where equilibrium is eventually achieved for concentrations of these metals in sulfate form in the solution. Furthermore, with regeneration of the various nitrogen gases coming off the reaction and converted back to nitric acid and nitrous acid. The amount of nitric acid introduced may also move downwardly to compensate for the 10 to 20% of nitrogen gases which cannot be converted back to nitric acid.

It is preferred that the reaction is carried out at a temperature in the range of 110°C up to the boiling point of the solution which is about 175°C. A preferred reaction temperature in the range of 120°C to 170°C and
5 most preferred range of 110°C to 150°.

It is appreciated that the process of this invention could be carried out in a batch reactor. However, with the volumes of ore or ore concentrate to be treated, it is preferred to have a continuous process. It is
10 understood that a variety of known systems are available in which a continuous reactor may be provided in which the reaction of this invention may be carried out. A suggested reaction scheme for a single continuous reactor 8 is shown in Figure 1. The feed which consists of the
15 usual form of metal concentrate or metal rich ore, is introduced through line 10 into a lower region 11 of the continuous reactor 12 which in this embodiment is the common form of the known Pachucha type reactor. A source of oxygen which may be pure oxygen, oxygen enriched air
20 or air is introduced through line 14 at inlet 15 and upwardly through the lower portion 16 of the reactor. The gases flow directly upwardly of the draft tube 18 to cause a circulation of the material within the reactor 12 in a direction of arrows 20. The necessary sulfuric
25 acid, nitric acid and reagents are introduced through line 22 in accordance with the process parameters as already described. The gases mix with the acids and reagents to draw them into the circulating reacting mixture within the annular portion 24 of the tank and as
30 well within the draft tube portion 26 of the tank. Any gases produced in the reaction which are not converted back to nitric and nitrous acid (HNO_3 and HNO_2) are removed from the upward portion 28 of the reactor and removed for treatment and recycle through line 30. As
35 already discussed, the off gases as required can be treated to render them environmentally safe for exhaust used in other related processes or treated with water and

oxygen to convert remaining NO_x gases to nitric acid and nitrous acid (HNO_3 and HNO_2). The oxygen is introduced at inlet 15 and the needed water is produced "in situ" of the reaction mixture in accordance with the

5 aforementioned reaction scheme. Based on the mass flow rate of feed through line 10, correspondingly a solution containing the reactants is removed from below liquid level at region 31 through vented overflow line 32 for further processing. The solution removed in line 32

10 includes the formed precipitate. The precipitate in the acidic solution is transferred through line 32 to a solid liquid separator 34. The liquid separated from the light and dark precipitate is removed via line 36 and recycled to the reactor 12 normally through line 22. The solid

15 which has most of the acid solution removed therefrom is transferred via line 38 to a centrifuge 40 or a filter press which removes the remainder of the acidic solution from the solid precipitate. The remaining acid solution is removed from the centrifuge via line 42 and recycled

20 to the reactor 12 through line 22. The moist solids are removed from the centrifuge 40 through line 44 or may be dumped from the centrifuge depending upon the choice thereof. It is understood that when necessary, a series of the continuous reactors 8 may be set up in a cascade

25 manner to treat the incoming concentrate to an extent which achieves the desired conversion of the sulfides into the insoluble copper and zinc sulfates. It is anticipated that in most applications, four reactors in series will be required. It should also be noted that

30 with respect to reactor design, that the Pachucha reactor normally has a height to diameter ratio of about 10:1.

The precipitate in the form of the moist solids, contains both the light and dark forms, where the valuable metals to be recovered from the light

35 precipitate can be recovered by leaching. A suggested technique for leaching the metals from the precipitate is by solvent extraction in accordance with a default

procedure. The default procedure involves the use of solvent extraction reagents. Copper can be extracted from a solution of pH around 2.5 using LIX 64N (a Heinkel reagent). The reagent is commonly used in heap leaching
5 of copper. Because the solutions are very acid, the solutions are partially neutralized with limestone and filtered to remove gypsum and iron compounds (goethite or jarosite) before extraction with solvent. The extraction solvent is then stripped and cut with spent electrolyte
10 which is strongly acid (typically 200 g) H_2SO_4 , and 35-40 g/L copper from the electrowinning cells before returning to the electrowinning cells to recover copper. The raffinate from the solvent extraction step contains residual copper, which can be cemented out with zinc
15 dust. The raffinate should be neutralized still further, to pH 4 to 5, before zinc extraction. Again, gypsum and iron oxide are filtered off before extraction. The zinc reagent used in the solvent extraction is Di-2 Ethyl Hexyl Phosphoric Acid (D2EHPA), and succeeds in
20 transferring zinc from this solution through the organic reagent into a zinc electrowinning solution to recover zinc. Other suitable reagents include (Cyanex 302, made by American Cyanamid).

With the preferred embodiment of the invention as
25 exemplified with respect to the use of the Pachucha reactor, it is apparent that a reaction mixture is established within the tank 12 primarily in regions 24 and 26. Sufficient acid and oxygen reagents and other processing agents are added to the reactor either as
30 needed or on a continuous basis to ensure that the desired optimum amount of light precipitate is continually produced and removed through line 32. It is appreciated that the solutions in which the copper and zinc are recovered are further processed by
35 electrowinning to refine the copper and zinc to the desired purity. By proper extraction of the copper and zinc from the precipitate, a minimum amount of iron is

present in the respective solutions so that iron does not interfere with the electrowinning processes.

Furthermore, in the extraction, the nitric acid remaining in the precipitate is minimized so as to have little if
5 any effect on the electrowinning processes. Any copper in the zinc electrowinning stream will be cemented out with Zn dust.

Preferred embodiments of the invention are exemplified in accordance with the following Examples.

10 EXAMPLE 1

Experimental Details

The Reactions have been run at sulfuric acid concentrations of 45%, 50%, 65% and 75% (by volume). All reactions have used 10 g of concentrate, 65 mL of
15 sulfuric acid solution, and 12 mL of nitric acid (conc.). The nitric acid was added over 20 minutes to the stirring reaction mixture which was held at 120°C to 130°C for one hour. The reaction was continually flushed with oxygen and the gaseous products absorbed or trapped over aqueous
20 sodium hydroxide solution. After one hour the reaction was further flushed for 30 minutes and the cooled reaction products weighed and vacuum filtered. The light coloured to white precipitate was dissolved in water. The residual black to dark precipitate was extracted with
25 carbon disulfide. The resulting dark gangue, the solution of white precipitate and the original filtrate was analyzed by atomic absorption spectroscopy. Titration of the aqueous sodium hydroxide solution gave a measure of the nitric acid recovered as nitrate or
30 nitrite.

Results

The sodium hydroxide solution indicates that a large amount of nitric acid nitrate is not appearing in the gas stream under the above conditions. The 75% sulfuric acid
35 filtrate bubbles off large quantities of brown gas upon dilution with water.

The nitric acid was added over extended periods. The longer the reaction times at lower temperatures results in more use of the oxygen present so that less nitric acid is required.

5 Analytical results for two experiments are set out in Table II. The results for the solution, white ppt. and gangue approximate by weight, approximately 100%. The results indicate that better extraction of copper to the white precipitate is achieved by the 50% sulfuric
10 acid reaction than the 65% sulfuric acid solution. This agrees with the weights of gangue reported in Table I where there is a trend of increasing gangue weight with increasing sulfuric acid strength.

15 The impact of the concentration of sulfuric acid on the amount of precipitate in its light and dark forms is demonstrated in the following Table III where concentrations of sulfuric acid range from 25% v/v to 75% v/v. At a concentration of about 35% v/v, there is a noticeable increase in weight of precipitate. This
20 increase indicates that the lowest H_2SO_4 concentration for this process is in the range of 35% v/v.

TABLE I
Weights of Reactants and Products

H ₂ SO ₄ (v/v)	Reactants (Wt. g)	Products (Wt. g)	Filtrate (Vol. mL)	(Wt. g)	Ppts. (Wt. g)	Gangue (Wt. g)	Sulfur (Wt. g)
45	120.7	114.8	44.5	64.5	46.6	0.707	1.47
50	124.6	117.1	38	57.7	49.2	0.798	1.52
65	130.4	125.6	49	75.9	43.5	1.151	2.01
75	136.3	131.9	45	72.9	49.8	1.78	1.81

TABLE II**Analytical Results ***

Sample	Material	Iron %	Copper %	Zinc %
99-0 #1	Concentrate	29.4	26.8	10.7
99-0 #2	Concentrate	29.4	26.4	10.4
99-0 #3	Concentrate	29.6	26.5	10.1
99-0 avg		29.5	26.5	10.4
99-1	50% solution	7.79	23.2	37.8
99-2	white ppt.	80.3	64.9	46.3
99-3	gangue	5.62	7.1	0
	total	93.8	95.2	84.1
102-1	65% solution	0.87	10.72	0.83
102-2	white ppt.	87.45	71.32	96.15
102-3	gangue	8.01	11.02	3.46
	total	96.35	93.1	100.4

*Results for reaction products are calculated as percentage of total amount of metal expected in the concentrate sample.

TABLE III**Weights of Reactants and Products**

H ₂ SO ₄ (v/v)	Reactants (Wt. g)	Products (Wt. g)	Difference (Wt. g)	Filtrate (Vol. mL)	Density (Wt. g)	Ppts. (Wt. g)	Gangue (Wt. g)	Sulfur (Wt. g)	
25	107.67	104.93	-2.74	70	97.2	1.39	5.67	0.598	1.68
35	113.79	112.33	-1.46	55	77.92	1.42	31.55	0.416	1.49
45	120.7	114.8	-5.9	44.5	64.5	1.45	46.6	0.707	1.47
50	124.6	117.1	-7.5	38	57.7	1.52	49.2	0.798	1.52
65	130.4	125.6	-4.8	49	75.9	1.55	43.5	1.151	2.01
75	136.3	131.9	-4.4	45	72.9	1.62	49.8	1.78	1.81

EXAMPLE 2

The process of this invention was carried out at two different sulfuric acid concentrations with dilute solutions of nitric acid based on the following results.

- 5 It is demonstrated that the amount of nitric acid required in the reaction mixture can be reduced providing there is presence of oxygen in the reaction mixture. Reactions were carried out using 40% and 50% sulfuric acid and in 6 mL and
- 10 3 mL of 70% nitric acid, respectively. The third reaction was run under oxygen and with 12 mL HNO₃ as usual but after one hour the oxygen was replaced with argon and the reaction vessel heated to reflux conditions of approximately 170°C for 30 minutes. The fourth reaction
- 15 was under argon for the entire time. After 30 minutes the temperature was raised to the reflux range of 175 to 180°C for 30 minutes. In this way the effect of oxygen and nitric acid concentration was determined. The results of these tests are summarized in following Table
- 20 IV.

TABLE IV**Weights of Reactants and Products**

H ₂ SO ₄ (v/v)	Reactants (Wt. g)	Products (Wt. g)	Difference (Wt. g)	Filtrate (Vol. mL)	Density (Wt. g)	Ppts. * (Wt.g)	Gangue* * (Wt. g)	Sulfur (Wt. g)	
40	107.03	107.29	0.26	34	49.4	1.45	~50	0.924	1.651
40	104.47	106.59	2.12	41.5	58.7	1.41	45.6	1.862	1.707
40	118.33	115.01	-3.32	64	92.5	1.44	~25	0.342	1.653
50	124.60	116.42	-7.64	60	89.0	1.48	23.7	~3.6	1.460

*Wet cake of vacuum filtered precipitate containing white precipitate and some or all of black precipitate.

**Carbon disulfide extracted black precipitate

From the results of the reactions with the reduced amount of nitric acid, it is apparent that conversion of the sulfides to sulfates is within an acceptable range to demonstrate thereby the ability to reduce the amount of
5 nitric acid present in the reaction mixture while at the same time maintaining the presence of oxygen in the reaction mixture.

Although preferred embodiments of the invention are described herein in detail, it will be understood by
10 those skilled in the art that variations may be made thereto without departing from the spirit of the invention or the scope of the appended claims.

CLAIMS:

1. A continuous hydrometallurgical process for conversion in the presence of nitric acid of copper and/or zinc sulfides into recoverable precipitates of their corresponding sulfates while minimizing emissions of nitrogen gas and N_2O gas, said process comprising:
 - i) contacting said copper and/or zinc sulfides obtained from said ores with sulfuric acid and nitric acid to form a reaction mixture in an acidic solution,
 - 10 ii) maintaining said reaction mixture at a temperature in the range of $110^{\circ}C$ to $170^{\circ}C$ while continuously mixing said reaction mixture,
 - iii) adding sufficient sulfuric acid and nitric acid to said reaction mixture to form a light coloured precipitate and a dark coloured precipitate in said reaction mixture, said light precipitate comprising water soluble sulfate salts of copper sulfate and/or zinc sulfate and said dark precipitate being water insoluble and comprising sulfur and gangue,
 - 20 iv) introducing a source of oxygen to said reaction mixture to promote oxidation in the presence of said nitric acid and sulphuric acid of said sulfides to sulfates and oxidize gaseous NO , reaction products to regenerate nitric acid for use in said reaction mixture,
 - 25 v) removing said light and dark precipitates and any entrained acidic solution from said reaction mixture,
 - vi) separating said light and dark precipitate from said acidic solution in preparation for treatment of said light precipitate for recovery of copper sulfate and/or zinc sulfate from said light precipitate, and
 - 30 vii) recycling said acidic solution to said reaction mixture.
2. A process of claim 1 wherein a finely divided ore concentrate comprising said copper and/or zinc sulfides is contacted with said sulfuric and nitric acids in said reaction mixture.

3. A process of claim 2 wherein said ore concentrate is derived from an ore body of chalcopyrite, sphalerite or other sulfide minerals.

5 4. A process of claim 3 wherein iron, as part of copper iron sulfide in said chalcopyrite ore concentrate, is converted in said reaction mixture to iron sulfate which in said acidic solution precipitates and thereby forms part of said light precipitates, said process converting
10 copper into said recoverable precipitate.

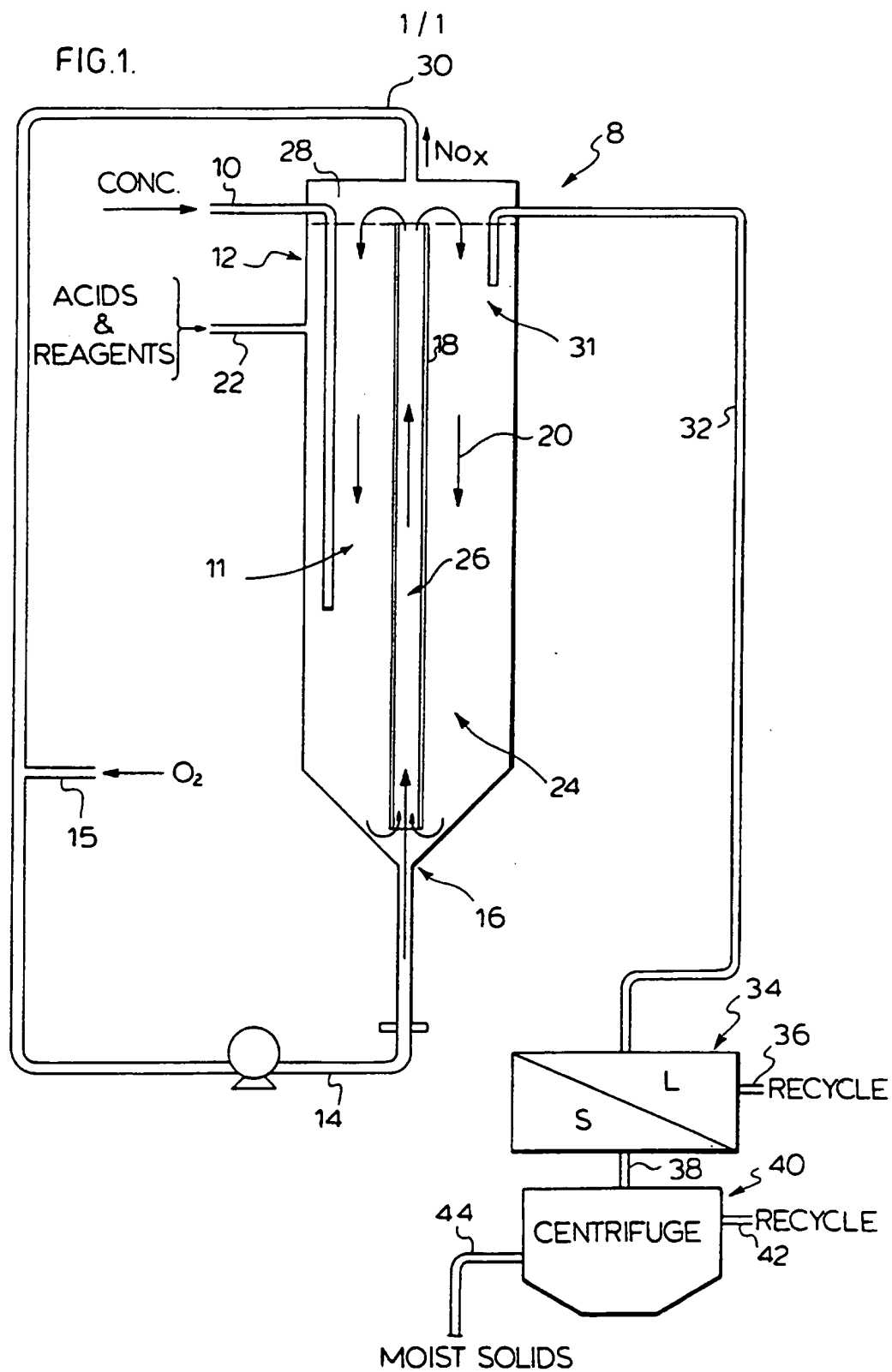
5. A process of claim 1 wherein sufficient sulfuric acid is added to said reaction mixture to maintain in said reaction mixture a volume concentrate of
15 concentrated sulfuric acid to volume of reaction mixture in the range of 35% to 65% volume per volume.

6. A process of claim 5 wherein sufficient nitric acid is added to said reaction mixture to maintain in said
20 reaction mixture a molar concentration of nitric acid of at least 0.5 moles of nitric acid per mole of copper sulfide.

7. A process of claim 6 wherein said molar
25 concentration of said nitric acid is in the range of 0.5 moles to 3 moles per mole of copper sulfide and said concentration of sulfuric acid is in the range of 40% to 65% volume per volume.

30 8. A process of claim 7 wherein copper and zinc are recovered from said combined dark and light precipitate by water treatment to dissolve and remove from said precipitate, the soluble copper sulfate and zinc sulfate salts.

FIG.1.



INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C22B3/44 C22B3/06 C22B3/08 C22B3/00 C22B15/00
 //C22B15:00,19:00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, L	WO, A, 92 15713 (ENVIRONCHIP TECHNOLOGIES LTD.) 17 September 1992 see page 1, line 1 - page 13, line 21; claims 1-5, 10, 14-17, 19-22, 30, 31; figure 1; example 2 "L": DOCUMENT SO QUOTED FOR IT'S CASTING DOUBT ON THE FIRST DEPOSIT CHARACTER OF US930009844 AND THUS VALIDITY OF THE CONVENTION-PRIORITY CLAIM ---	1-8
P, X, L	DATABASE WPI Derwent Publications Ltd., London, GB; AN 94-057795 & CA, A, 2 070 315 (O'BRIEN, R. N.) 4 December 1993 see abstract --- -/--	1

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Date of the actual completion of the international search

8 April 1994

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMISTRY AND INDUSTRY 20 June 1981 pages 427 - 431 DOUGLAS S. FLETT 'THE ROLE OF HYDROMETALLURGY IN EXTRACTIVE METALLURGY' ---	
A	FR,A,2 190 928 (E.I. DU PONT DE NEMOURS AND COMPANY) 1 February 1974 see page 1, line 1 - page 16, line 25; claims 1-9 & US,A,3 888 748 (H.M. BRENNECKE) 10 June 1975 cited in the application ---	1-4,6,7
A	EP,A,0 119 685 (M.J.A. VREUGDE ET AL.) 26 September 1984 & US,A,4 647 307 (MORRIS J. A. VREUGDE ET AL.) 3 March 1987 cited in the application ---	
A	EP,A,0 113 649 (BOLIDEN AB) 18 July 1984 ---	
A	EP,A,0 272 060 (ELECTROLYTICZINC COMPANY OF AUSTRALIA LTD) 18 December 1988 ---	
A	EP,A,0 166 710 (SOCIETE DES MINES & FONDERIES DE ZINC DE DELA VIEILLE MONTAGNE S.A.) 28 May 1984 ---	
A	US,A,4 132 758 (TH.C. FRANKIEWICZ ET AL.) 2 January 1979 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Appl. Application No

PCT/CA 94/00034

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9215713	17-09-92	US-A- 5188713	23-02-93
		AU-A- 1333092	06-10-92
		EP-A- 0574463	22-12-93
FR-A-2190928	01-02-74	US-A- 3888748	10-06-75
		AU-A- 5764173	09-01-75
		CA-A- 1027894	14-03-78
		DE-A, B 2332937	31-01-74
		GB-A- 1407520	24-09-75
		JP-C- 1069103	23-10-81
		JP-A- 49056818	03-06-74
		JP-B- 55051017	22-12-80
		JP-A- 52148418	09-12-77
		NL-A- 7309048	02-01-74
		BE-A- 811653	27-08-74
		JP-A- 49072122	12-07-74
US-A-3888748	10-06-75	AU-A- 5764173	09-01-75
		BE-A- 811653	27-08-74
		CA-A- 1027894	14-03-78
		DE-A, B 2332937	31-01-74
		FR-A, B 2190928	01-02-74
		GB-A- 1407520	24-09-75
		JP-C- 1069103	23-10-81
		JP-A- 49056818	03-06-74
		JP-B- 55051017	22-12-80
		JP-A- 52148418	09-12-77
EP-A-0119685	26-09-84	NL-A- 7309048	02-01-74
		AU-B- 566135	08-10-87
		AU-A- 2351584	19-07-84
		CA-A- 1219132	17-03-87
		DE-A- 3473163	08-09-88
		US-A- 4647307	03-03-87
US-A-4647307	03-03-87	AU-B- 566135	08-10-87
		AU-A- 2351584	19-07-84
		CA-A- 1219132	17-03-87
		DE-A- 3473163	08-09-88
		EP-A, B 0119685	26-09-84

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 94/00034

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0113649	18-07-84	SE-B- 451463	12-10-87
		AU-B- 558324	29-01-87
		AU-A- 2101983	14-06-84
		CA-A- 1224926	04-08-87
		JP-A- 59110739	26-06-84
		SE-A- 8207053	10-06-84

EP-A-0272060	22-06-88	JP-A- 63166935	11-07-88

EP-A-0166710	02-01-86	LU-A- 85385	29-01-86
		AU-B- 575944	11-08-88
		AU-A- 4271385	05-12-85
		CA-A- 1258180	08-08-89
		DE-A- 3564450	22-09-88
		JP-A- 60255938	17-12-85
		US-A- 4676828	30-06-87

US-A-4132758	02-01-79	CA-A- 1110077	06-10-81
		CA-A- 1110076	06-10-81
		US-A- 4189461	19-02-80

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